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Indian Standard

MINERAL INSULATING OILS — METHODS FOR THE DETERMINATION OF 2-FURFURAL AND RELATED COMPOUNDS

ICS 17.220.99; 29.040.10

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BUREAU OF INDIAN STANDARDS
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NEW DELHI 110002

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NATIONAL FOREWORD

This Indian Standard which is identical with IEC 61198 (1993) 'Mineral insulating oils — Methods for the determination of 2-furfural and related compounds' issued by the International Electrotechnical Commission (IEC) was adopted by the Bureau of Indian Standards on the recommendation of the Fluids for Electrotechnical Applications Sectional Committee and approval of the Electrotechnical Division Council.

The text of the ISO Standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words 'International Standard' appear referring to this standard, they should be read as 'Indian Standard'.

b) Comma (,) has been used as a decimal marker while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

In this adopted standard, reference appears to certain International Standards for which Indian Standards also exist. The corresponding Indian Standards which are to be substituted in their respective places are listed below along with their degree of equivalence for the editions indicated:

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
IEC 475 (1974) Method of sampling liquid dielectrics	IS 6855 : 2003 Method of sampling for liquid dielectrics (*first revision*)	Technically Equivalent
IEC 567 (1992) Guide for the sampling of gases and of oil from oil-filled electrical equipment and for the analysis of free and dissolved gases	IS 9434 : 1992 Guide for the sampling and analysis of free and dissolved gases and oil from oil-filled electrical equipment (*first revision*)	do

Only the English text of the International Standard has been retained while adopting it as an Indian Standard and as such the page numbers given in IEC Standard are not the same.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

IS 15668 : 2006
IEC 61198 (1993)

Indian Standard

MINERAL INSULATING OILS — METHODS FOR THE DETERMINATION OF 2-FURFURAL AND RELATED COMPOUNDS

1 Scope

This International Standard specifies test methods for the analysis of 2-furfural and related furan compounds resulting from the degradation of cellulosic insulation and found in mineral insulating oil samples taken from electrical equipment.

2-furfural and related furan compounds dissolved in mineral oil are analysed by high performance liquid chromatography (HPLC). Prior to HPLC analysis, furan derivatives are extracted from the oil by use of a suitable extraction method such as liquid-liquid extraction (method A) or solid-phase separation on a silica cartridge (method B).

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication of this standard, the editions indicated were valid. All normative documents are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

IEC 475: 1974, *Method of sampling liquid dielectrics*

IEC 567: 1992, *Guide for the sampling of gases and of oil from oil-filled electrical equipment and for the analysis of free and dissolved gases*

3 Sampling

Oil samples are collected in accordance with IEC 475 and IEC 567. Samples should be protected from direct light.

4 Labelling of samples

Samples shall be labelled in accordance with IEC 567.

5 Apparatus

5.1 *General equipment:*

- laboratory glassware;
- beakers or Erlenmeyer flasks;
- volumetric flasks;
- pipettes;
- analytical balance (0,1 mg).

5.2 *Equipment for extraction by method A*

- 25 ml glass stoppered graduated cylinder;
- 5 ml pipette;
- mechanical shaker.

5.3 *Equipment for extraction by method B*

- silica cartridges, containing about 1 g of silica with a particle size ranging from 15 µm to 100 µm. Commercially available cartridges are suitable;
- a vacuum device suitable to produce a slight vacuum (i.e. filter pump or vacuum manifold), see figure 1;
- a 10 ml luer lock syringe;
- volumetric flasks, 2 ml.

5.4 *High-performance liquid chromatograph (HPLC)*

A high-performance liquid chromatograph equipped with:

- pumping system suitable for at least two solvents;
- injection device capable of injecting 10 µl to 20 µl and suitable precision syringe (50 µl to 250 µl);
- reversed phase column packed with octyl or octadecyl bonded silica;
- pre-column packed with the same material as the analytical column (optional);
- UV detector capable of recording UV spectra; a diode array UV detector is recommended;
- data acquisition system (recorder or integrator).

6 Reagents

- HPLC grade acetonitrile;
- HPLC grade methanol;
- HPLC grade water;
- HPLC grade acetic acid;
- Analytical grade n-pentane;
- Analytical grade analytes as listed in clause 8.

7 Symbols and units

F_i Detector response factor for each of the analytes.

R_s^i Detector response for each analyte in the calibration standards (the response may be expressed by peak area or peak height).

R_i Detector response for each of the detected analytes.

C_s^i ($mg \cdot kg^{-1}$) Concentration of each analyte in the calibration standards.

C_i ($mg \cdot kg^{-1}$) Concentration of each of the analytes in the mineral insulating oil sample.

8 Analytes

Analytical conditions shall be suitable for the determination of the following furan derivatives:

– 5-hydroxymethyl-2-furfural	(5HMF)
– 2-furfurylalcohol	(2FOL)
– 2-furfural	(2FAL)
– 2-acetylfuran	(2ACF)
– 5-methyl-2-furfural	(5MEF)

For the purpose of this standard the determination of furoic acids is optional as it is often difficult to resolve them from other organic acids that may be present in aged mineral insulating oil samples.

9 Operating procedure

9.1 *Extraction of the analytes*

9.1.1 *Method A: liquid-liquid extraction*

Extract approximately 20 ml of oil sample, wheighed to the nearest 0,1 g, with 5 ml of acetonitrile, measured by a pipette, in a 25 ml stoppered cylinder, shaking the samples on a mechanical shaker for at least 2 min.

Allow the samples to stand until the solvent and oil layers separate completely. The extract can then be analysed as described in 9.2.

NOTE - The time period necessary for phase separation tends to increase for oils with higher acid values.

9.1.2 *Method B: solid-liquid extraction*

Weigh exactly 10 g ± 0,1 g of oil sample and dissolve it in 10 ml analytical grade n-pentane.

Rinse a new silica cartridge with 2 ml n-pentane and discard the eluate. While the silica is still wet, immediately pass the sample solution through the cartridge under a slight vacuum at a maximum flow of 3 ml/min followed by 20 ml n-pentane. Discard all eluates.

Dry the cartridge by suction by maintaining the vacuum for at least 5 min.

Release the vacuum and elute the retained material with the same eluent used in the first minutes of the chromatogram (see 9.2), using a 10 ml syringe as the dispenser.

Collect the first two millilitres in a 2 ml volumetric flask.

NOTE - Annex A describes a method to assess the efficiency of the silica cartridge.

9.2 *Analysis of the extract*

9.2.1 Adjust the liquid chromatograph in accordance with the manufacturer's instructions and establish suitable operating conditions.

9.2.2 The following set of conditions has been found satisfactory but some adjustments may be appropriate depending upon specific features of the instrumentation and local conditions.

- isocratic conditions;
- eluent: water 60 % to 80 % in volume;
  methanol or acetonitrile 20 % to 40 % in volume;
- flow rate: 0,5 to 2,0 ml/min.

NOTE - In some cases an elution gradient may be useful to improve the separation. Also the addition of a small amount of acetic acid (0,01 %) may improve the separation of the more polar compounds.

9.2.3 The UV detector shall monitor the following wavelengths:

220 nm for 2-furfurylalcohol.

275 nm to 280 nm for all other compounds listed in clause 8.

NOTE - Maximum light absorption occurs at approximately the following wavelengths:

– 5-hydroxymethyl-2-furfural	280 nm
– 2-furfurylalcohol	215 nm
– 2-furfural	274 nm
– 2-acetylfuran	272 nm
– 5-methyl-2-furfural	288 nm

Selection of the above wavelengths will enhance the sensitivity of the analysis for specific compounds.

9.2.4 When the chromatograph and detector are equilibrated inject an aliquot of the extract and record the detector response. Examples of typical chromatograms are shown in figure 2.

9.2.5 After elution of the last peak of interest (5-methyl-2-furfural with specified columns) switch the mobile phase to 100 % methanol or acetonitrile and increase the flow rate until all oil residues have been flushed out of the column.

10 Calibration

Standard solutions in oil are required to calibrate analyses of extracts obtained from method A.

Standard solutions either in oil or in chromatographic eluent may be used with extracts prepared in accordance with method B.

10.1 *Standard solutions in oil*

10.1.1 *Preparation of stock solution*

- dissolve 0,025 g of each of the five compounds in 25 ml toluene (concentration 1 000 mg/l);
- stock solutions shall be stored in a brown glass bottle and kept in the dark. They should be replaced at intervals of not more than three months.

10.1.2 *Preparation of standard solutions*

- dilute an aliquot of the toluene stock solution in a weighed amount of unused mineral insulating oil to prepare a standard solution of the desired concentration (i.e. 0,5, 1,0, 5 or 10 mg/kg);
- store in brown glass bottles and keep in the dark.

NOTES

1 Select an appropriate mineral insulating oil which is free from species likely to interfere with the analytes.

2 Standard solutions deteriorate rapidly if they are not properly stored. Freshly-prepared solutions are preferred.

10.2 *Standard solution in the chromatographic eluent*

If method B is used, an alternative easier and faster calibration procedure may be used:

- weigh 0,015 g of each of the five compounds;
- dissolve them in 100 ml of the chromatographic eluent to obtain a stock solution of about 150 mg/l;
- dilute the stock solution to obtain a standard solution of the desired concentration (i.e. 2,5, 5, 25 and 50 mg/l).

NOTE - Due to the concentration factor introduced by this method, a standard solution of, for example, 5 mg/l in methanol/water is equivalent to a concentration of 1 mg/kg in the oil.

10.3 *Procedure*

Extract and analyse the standard solutions prepared in oil (10.1) following the procedures described in clause 9.

Alternatively, analyse the standard solutions prepared in chromatographic eluent (10.2) following the procedure described in 9.2.

Four standard solutions in the concentration range 0,5 to 10 mg/kg are recommended to obtain a calibration line which should normally be a straight line through the origin. Experience has indicated that for everyday routine work a single point calibration at 1 mg/kg in oil is satisfactory.

NOTE - See note 2 of 10.1.2.

Identify each peak in the chromatogram by its retention time and UV spectrum. For guidance, typical UV spectra are shown in figure 3 but their appearance may change slightly depending on the particular instruments.

Calculate the response factor F_i of each analyte as follows:

$$F_i = \frac{C_s^i}{R_s^i}$$ for standard solutions in oil

$$F_i = \frac{C_s^i}{5R_s^i}$$ for standard solution in chromatographic eluent

where

C_s^i is the concentration of analyte i in the standard solution mg/kg (oil) s or mg/l (chromatographic eluent).

R_s^i is the response of the detector (peak area or peak height) of analyte i.

11 Calculations

Identify each peak in the sample chromatogram from its retention time and UV spectrum.

Measure the detector response (peak area or peak height) of each identified peak and calculate the concentration in oil as follows:

$$C_i = F_i \times R_i$$

where

C_i is the concentration of analyte i in the oil (mg/kg oil)

F_i is the response factor of analyte i

R_i is the detector response of the peak relative to analyte i

12 Report

The report shall include the following items:

- number of this standard;
- method of extraction and type of calibration used;
- identification of the sample;
- concentration of each analyte expressed in mg/kg to the nearest 0,01 mg/kg.

13 Minimum level of detection

Following the methods described in clause 9, the minimum concentration of the five analytes which can be determined in unused mineral oil shall be 0,05 mg/kg or lower.

In considerably oxidized samples the presence of polar compounds having similar retention times to the analytes may cause uncertainties in establishing a proper baseline and then the above detection limit may not be achieved.

14 Precision

14.1 *Repeatability*

When the method is correctly applied there is 5 % probability that the difference between two results obtained from two tests performed on the same oil under the same conditions (same operator, same apparatus, same laboratory and short interval of time) will exceed the values given in the following table:

Concentration of furan compounds	Value of repeatability in %
< 1,0 mg/kg	10
≥ 1,0 mg/kg	5

NOTE - In aged oils these values may not be achieved due to interferences with ageing products.

14.2 *Reproducibility*

When the method is correctly applied there is 5 % probability that the difference between two single and independent results obtained by different operators working in different laboratories on identical oil will exceed the values given in the following table:

Concentration of furan compounds	Value of repeatability in %
< 1,0 mg/kg	15
≥ 1,0 mg/kg	10

Annex A
(normative)

Checking extraction and recovery

Method B assumes complete retention of the analytes by the silica cartridge and complete recovery upon elution with HPLC eluent.

It is, however, good practice to evaluate the performance of the cartridges from batch to batch and the performance of the method with strongly oxidized oils in which the more polar compounds may be retained in preference to the analytes on the cartridge.

A.1 Checking extraction

Test the cartridge for retention efficiency following the procedure described in clause 9.1.2 but retaining the n-pentane eluates. Re-filter the eluate through a second, new cartridge, extract the cartridge and analyse by HPLC.

The chromatogram of this second extract must indicate the absence of any of the five analytes.

If the chromatogram indicates the presence of analytes during the analysis of strongly oxidized oils, it can be due to the presence of large amounts of polar compounds. In such a case the amount of mineral oil to be analysed shall be reduced.

If there are doubts about the performance of the cartridge batch, check the extraction procedure using a standard solution of analytes in unused mineral oil.

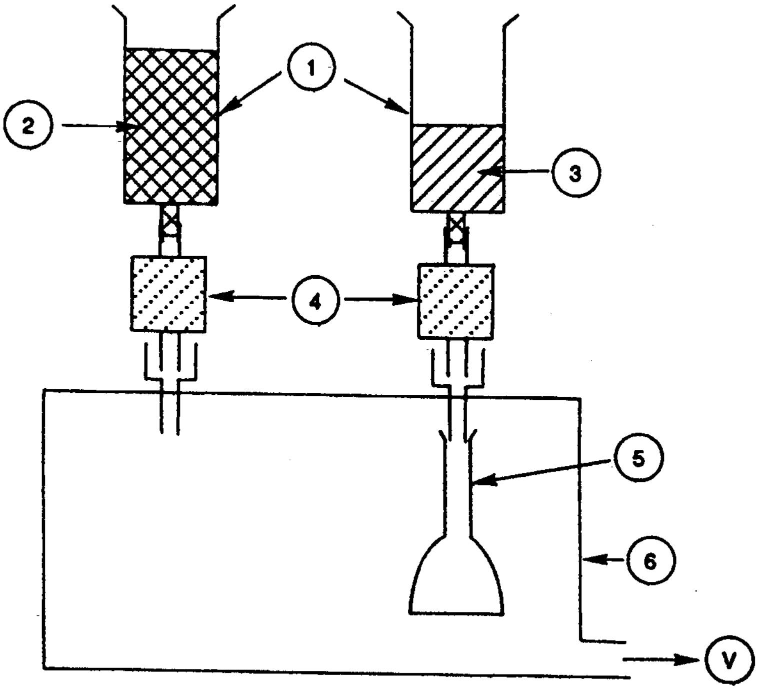
A.2 Checking recovery

To ensure that all the analytes retained in the cartridge have been recovered with HPLC eluent proceed as follows:

Once the cartridge has been eluted with HPLC eluent, dry it with air for at least 10 min, elute with pure methanol and analyse by HPLC.

The chromatogram must indicate the absence of any of the analytes. A positive result indicates that the amount of water in the mixture with HPLC eluent is excessively high or the cartridge is unsuitable for this method because the silica is excessively activated.

A more rapid procedure consists of collecting sequentially two separate 2 ml portions from the same extraction. This procedure gives information only about the irregular activity of the silica.



① Syringe

② Oil solution in pentane

③ Chromatographic eluent

④ Silica cartridge

⑤ Volumetric flask, 2 ml

⑥ Vacuum manifold

Ⓥ Connection to vacuum

Figure 1 –

Example of suitable device for extraction with silica cartridge (method B)

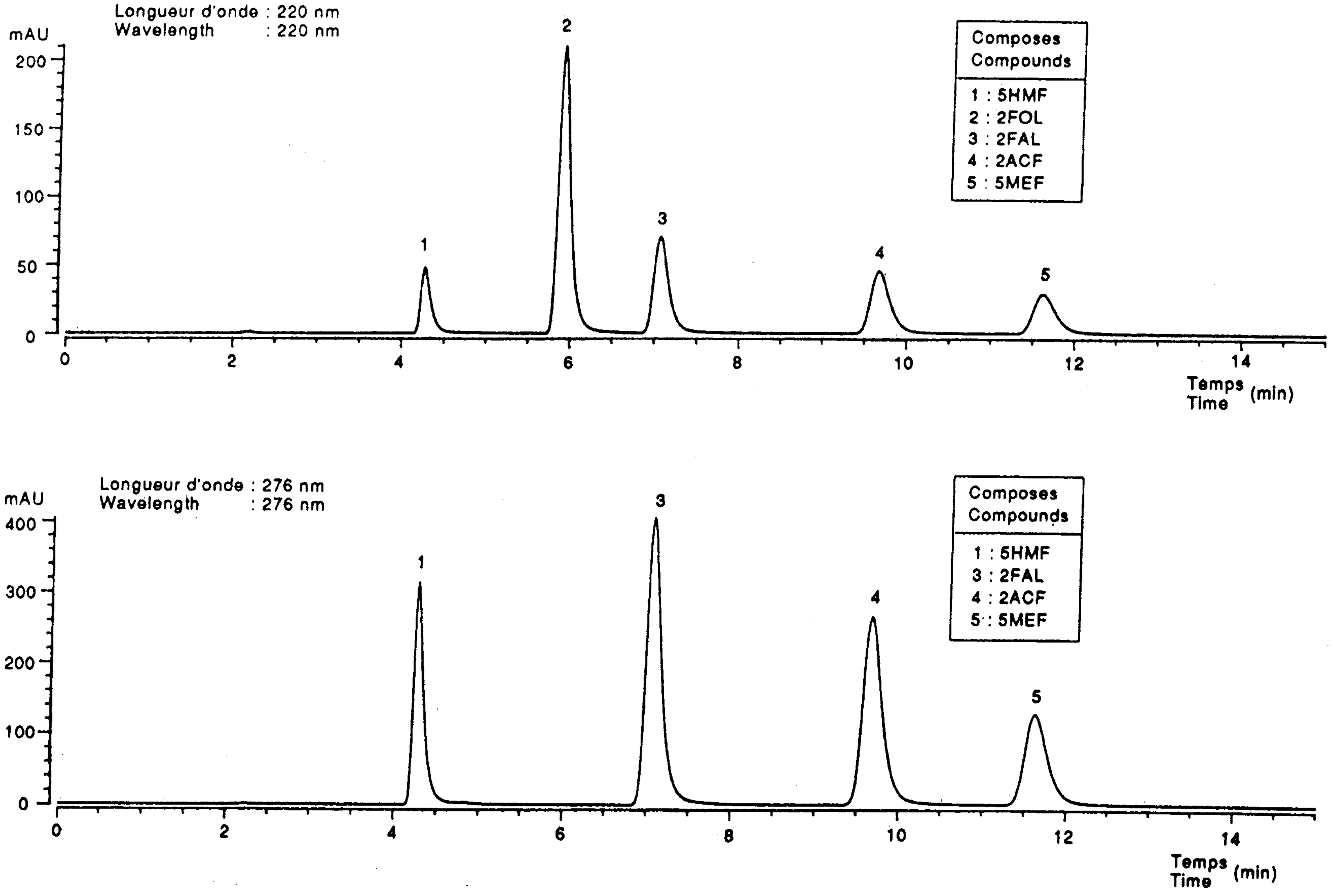


Figure 2 –

Examples of chromatograms recorded at two wavelengths (220 nm and 276 nm)

Captions to figure 2

Analytical conditions used to obtain the chromatograms given in figure 2

- Column reversed phase: C18
  particle size: 5 µm
  Length: 250 mm
  inner diameter: 4,6 mm
- Injected volume: 10 µl

HPLC conditions

Solvent A: water

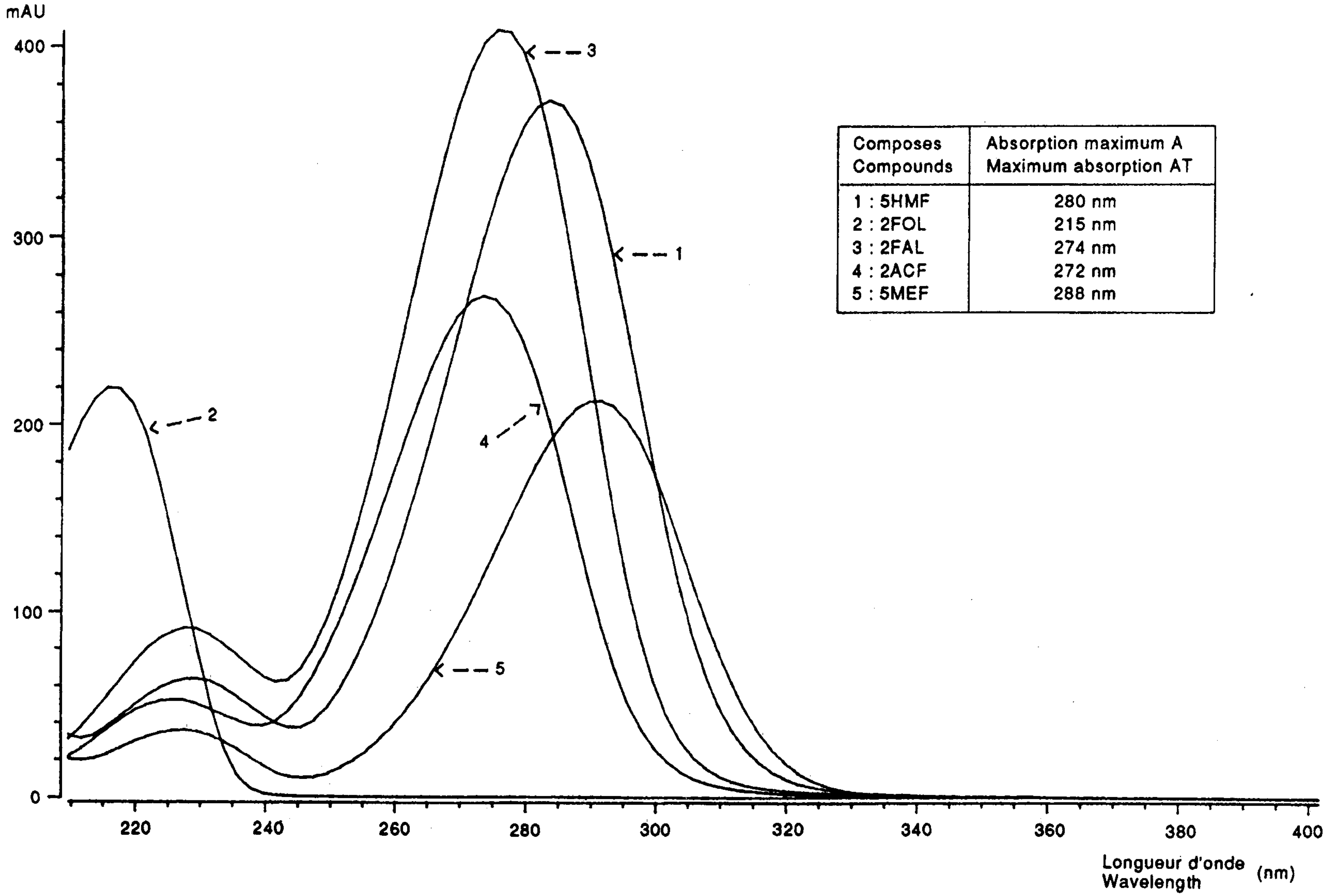
Solvent B: methanol

Liquid timetable

Time	
00,00 – 15,00	flow: 0,750 ml/min solvent A: 60 % B: 40 %
15,01 – 25,00	flow: 0,750 ml/min to 1,000 ml/min solvent A: 0 % B: 100 %
25,01 – 30,00	flow: 1,000 ml/min to 0,750 ml/min solvent A: 60 % B: 40 %

Concentrations of analytes in oil: 3 mg/kg

Method of extraction: Method B



Composes Compounds	Absorption maximum A Maximum absorption AT
1 : 5HMF	280 nm
2 : 2FOL	215 nm
3 : 2FAL	274 nm
4 : 2ACF	272 nm
5 : 5MEF	288 nm

Figure 3 –

UV spectra of the 2-furfural derivates

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Amendments Issued Since Publication

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